

Electronic Supplementary Information

β -cyclodextrin and cucurbit[7]uril as protective encapsulation agents of the CO-releasing molecule [CpMo(CO)₃Me]

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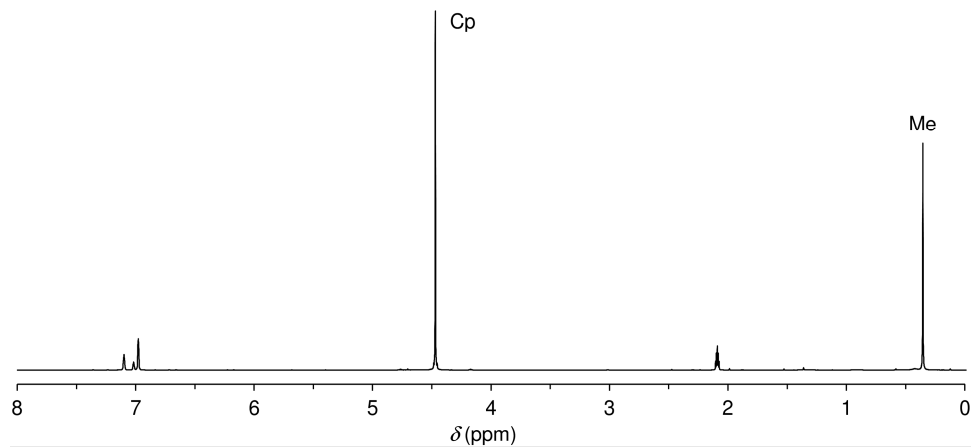


Fig. S1 ^1H NMR spectrum of **1** in toluene- d_8 .

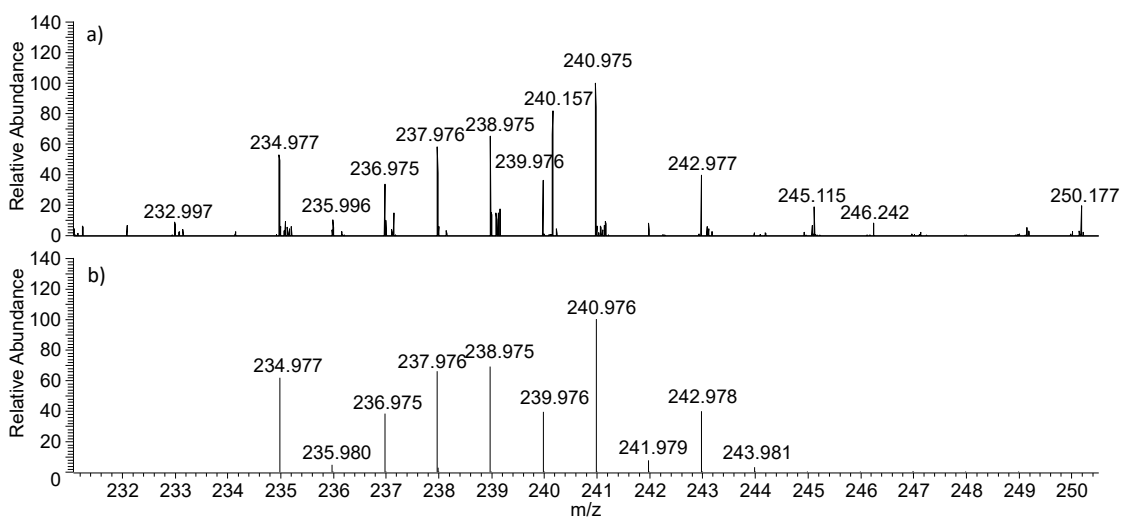


Fig. S2 Experimental, a), and simulated, b) ($\text{C}_7\text{H}_{11}\text{O}_3^+$), spectra between m/z 230 and 250 of an ethanol solution of **1**. Positive ESI.

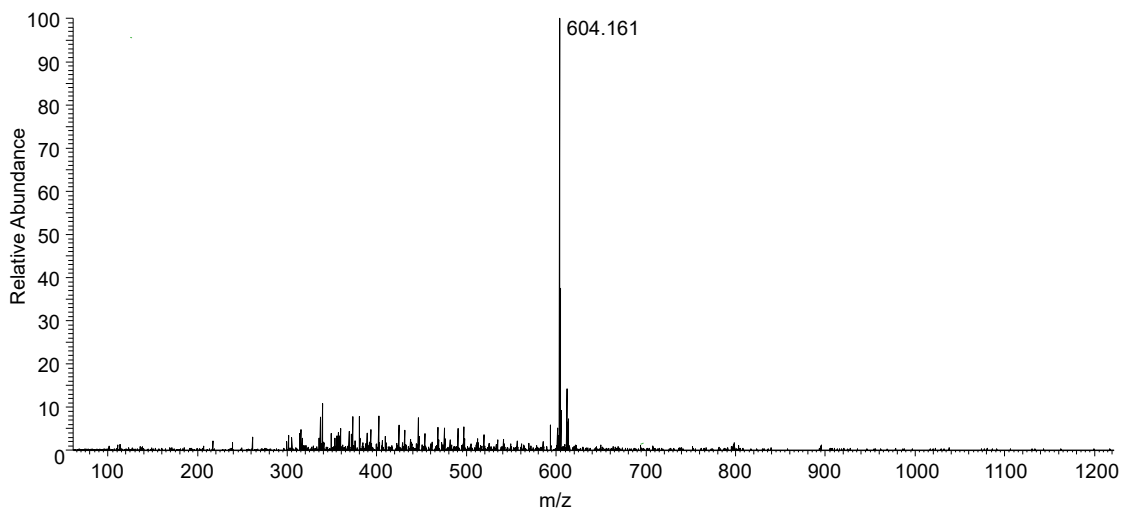


Fig. S3 ESI-HRMS spectrum (positive polarity) of CB7 in aqueous solution ($50\ \mu\text{M}$).

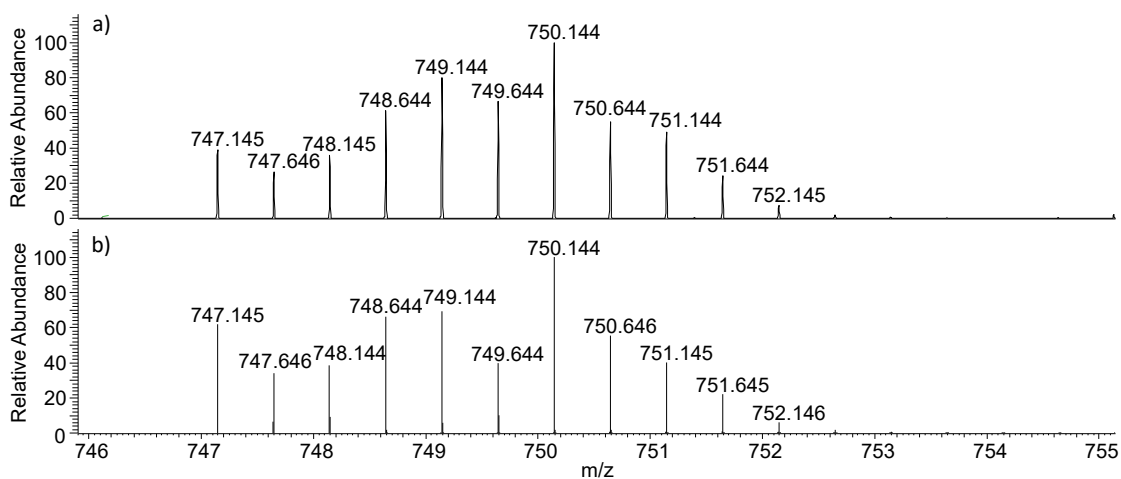


Fig. S4 Experimental, a), and simulated, b), $[\text{C}_{51}\text{H}_{55}\text{MoN}_{26}\text{O}_{19}\text{K}]^{2+}$, spectra between m/z 746 and 755 of aqueous **1**@CB7 complexes. Positive ESI.

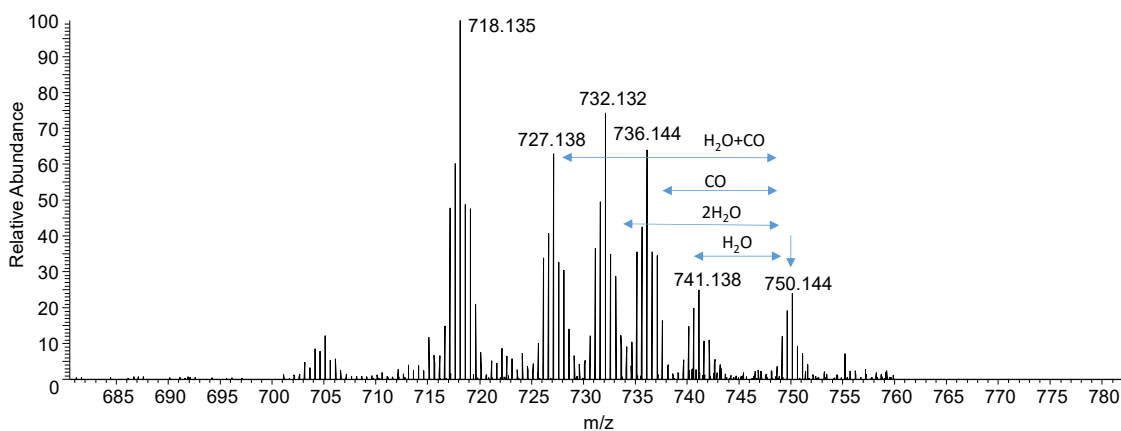


Fig. S5 Fragmentation spectrum (CID) of m/z 750 ($\Delta m/z=10$), assigned to $[\text{CB7}+\mathbf{1}+2\text{H}_2\text{O}+\text{H}+\text{K}]^{2+}$ spectrum of a saturated aqueous solution of **1** and CB7 (50 μM). Positive ESI.

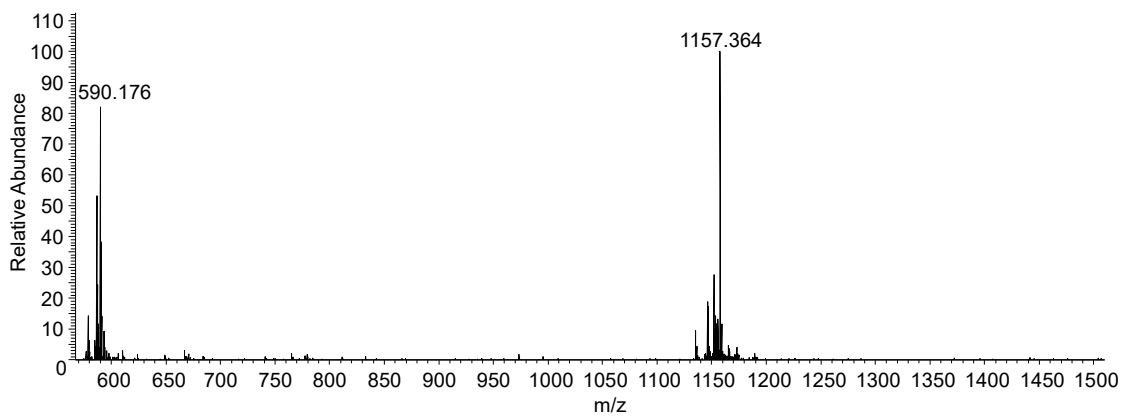


Fig. S6 ESI-HRMS spectrum (positive polarity) of a saturated aqueous solution of **1** and βCD (50 μM).

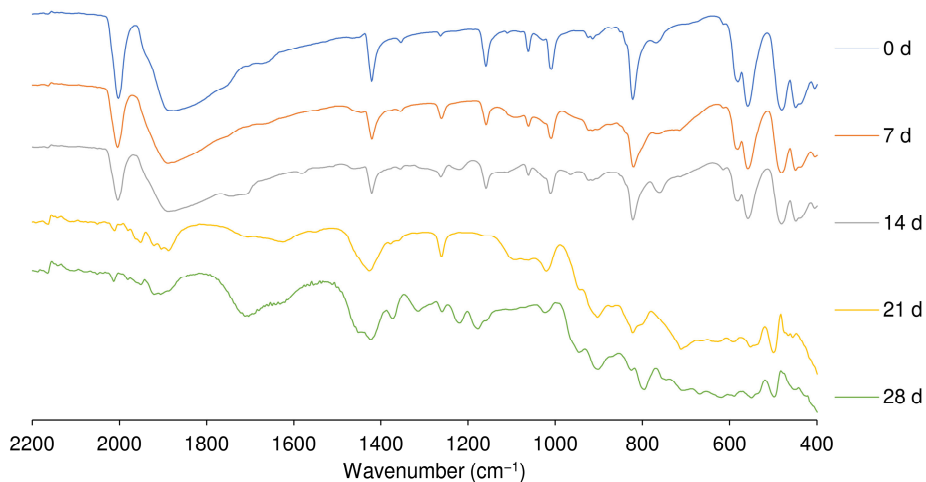


Fig. S7 ATR FT-IR spectra of solid **1** after exposure to ambient air and light for 0 to 28 days.

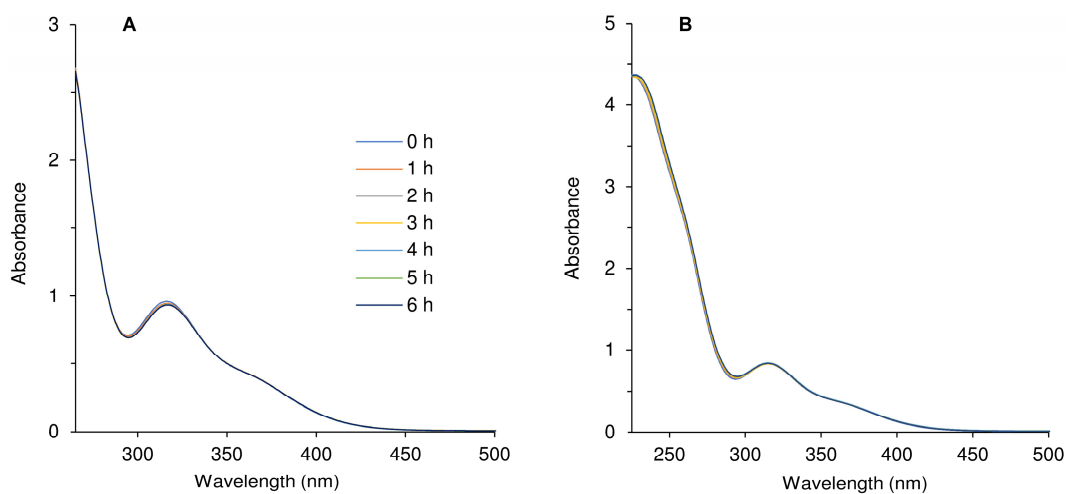


Fig. S8 UV-vis spectra measured over 6 h of complex **1** ($400\ \mu\text{M}$) in degassed (A) DMSO and (B) EtOH.

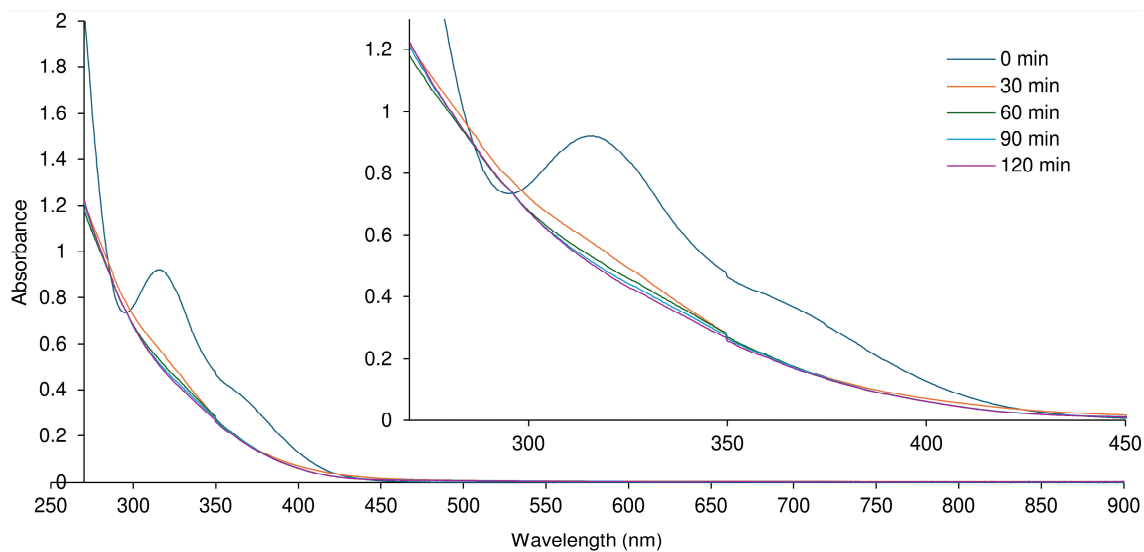


Fig. S9 UV-vis spectra of **1** in degassed DMSO ($400\ \mu\text{M}$) over 2 h with exposure to UV light (365 nm).

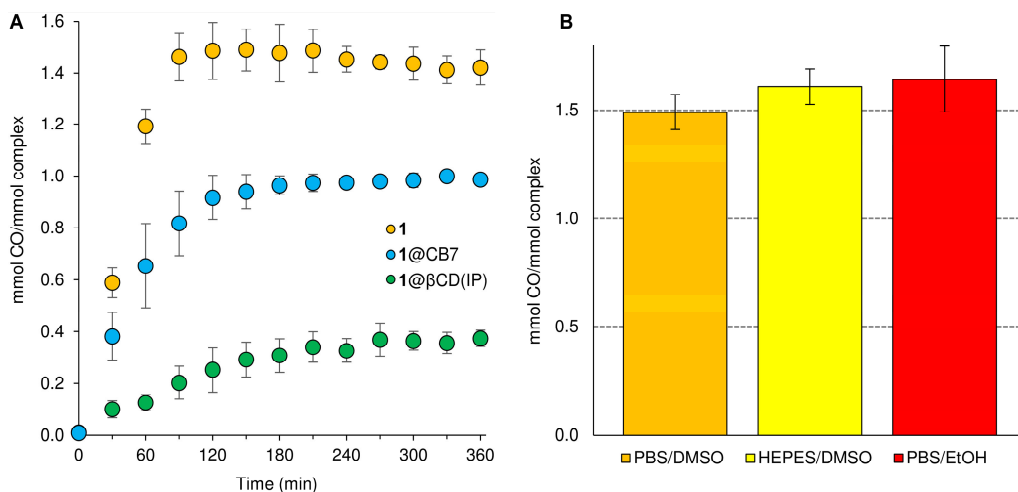


Fig. S10 (A) CO release profiles in the dark for 20 μ M solutions of complex **1**, **1**@ β CD(IP) and **1**@CB7 (DMSO as delivery solvent, 10 mM PBS, 0.4% sodium dithionite, pH 7.4, 37 $^{\circ}$ C). (B) Maximum amounts of CO released from **1** in Mb assays performed in the dark using different buffers (10 mM PBS or HEPES, 0.4% sodium dithionite, pH 7.4, 37 $^{\circ}$ C) and cosolvents (DMSO or ethanol). The data values are the mean \pm standard deviation of three independent assays.

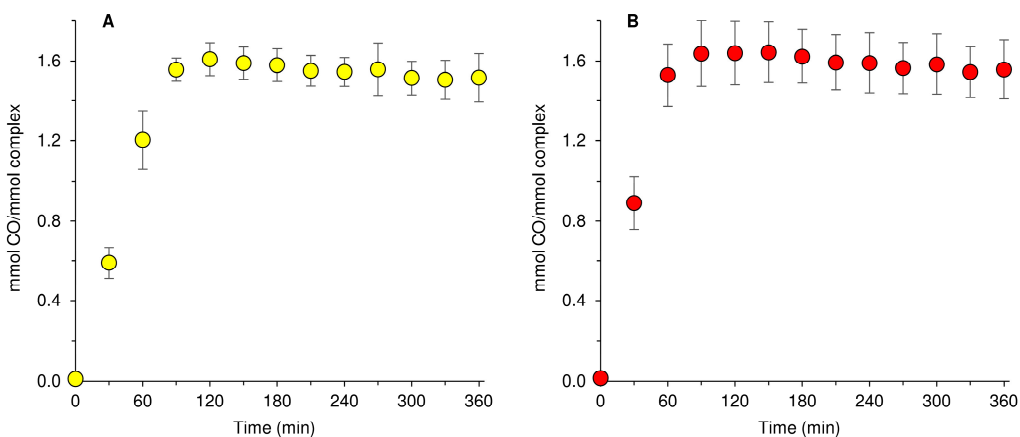


Fig. S11 CO release profiles obtained in the dark for 20 μ M solutions of complex **1** (0.4% sodium dithionite): (A) DMSO as delivery solvent, 10 mM HEPES, pH 7.4, 37 $^{\circ}$ C; (B) EtOH as delivery solvent, 10 mM PBS, pH 7.4, 37 $^{\circ}$ C. The data values are the mean \pm standard deviation of three independent assays.

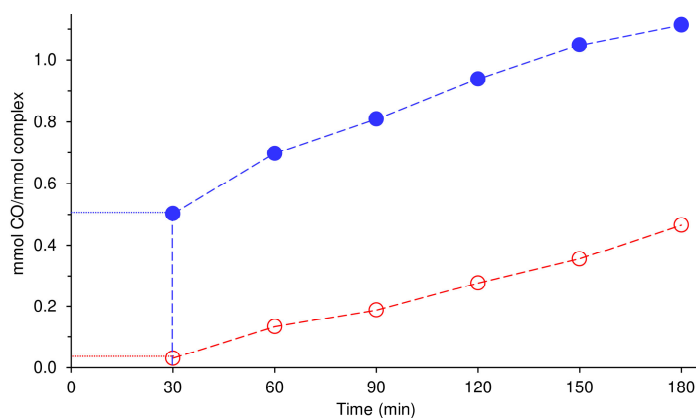


Fig. S12 Time courses of CO release from **1** (20 μ M) at 37 $^{\circ}$ C and in the dark (DMSO as delivery solvent, 10 mM PBS, 0.4% sodium dithionite, pH 7.4, 37 $^{\circ}$ C). Closed circles show the effect of adding Mb 30 min after **1** and dithionite. Open circles show the effect of adding Mb and dithionite 30 min after **1**. Horizontal dotted lines represent the amount of free CO in solution on the addition of Mb.